

P.G. Sem III

MPHYCC11

Condensed Matter Physics

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The Tight Binding Approximation - Extension to Three Dimensions

The extension of the tight binding (TB) approximation to three dimensions is straightforward and can easily be done based on the equations derived for tight binding approach.

The Schrödinger equation in one dimension is as follows:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E_0 - U(x)] \psi = 0 \quad \rightarrow (1)$$

In three dimensions, this eqn. can be written as

$$\nabla^2\psi + \frac{2m}{\hbar^2} [E_0 - U(\vec{r})] \psi = 0 \quad \rightarrow (2)$$

where ∇ is the Laplacian operator. In spherical polar coordinates

$$\nabla^2\psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial\psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2}$$

Here $U(r)$ is the potential energy of an electron in a free atom and the vector r corresponds now to position vectors. E_0 is the energy of an s state with wave function $\psi(r)$, which depends only on the radial coordinate. Next take an electron in the lattice of ions, its potential energy due to the ion at R_n being $U(r - R_n)$. The total potential energy in one dimension is

$$U(x) = \sum_n U(x - R_n) \quad \rightarrow (3)$$

In three dimension, this corresponds to

$$V(\vec{r}) = \sum_n U(\vec{r} - \vec{R}_n) \rightarrow (4)$$

the sum being over all the lattice points. The Schrodinger equation then becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - \sum_n U(\vec{r} - \vec{R}_n)] \psi = 0 \rightarrow (5)$$

The basic feature of tight Binding approach regarding the negligible overlap we can take the functions $\phi(\vec{r} - \vec{R}_n)$ centered on different lattice points to have hardly any overlap and hence approximate solutions of Eq. (5) to be of the Linear combination of Atomic Orbitals type. Thus we have;

$$\psi(\vec{r}) = \sum c_n \phi(\vec{r} - \vec{R}_n)$$

Compare above with Eq. (3).

Again as in one dimension, we can again choose the coefficients to be chosen so that the functions satisfy the Bloch conditions. Therefore;

$$\psi_k(\vec{r} + \vec{R}_n) = \sum_l \exp(i\vec{k} \cdot \vec{R}_l) \phi(\vec{r} - \vec{R}_l + \vec{R}_n)$$

$$= \exp(i\vec{k} \cdot \vec{R}_n) \sum_l \exp(i\vec{k} \cdot (\vec{R}_l - \vec{R}_n))$$

$$\phi[\vec{r} - (\vec{R}_l - \vec{R}_n)] \rightarrow (6)$$

$$\psi_k(\vec{r} + \vec{R}_n) = \exp(i\vec{k} \cdot \vec{R}_n) \psi_k(\vec{r}) \rightarrow (7)$$

We can for the sake of normalisation again ignore overlap

between atomic functions centred on different lattice points and assume that these functions are normalised in the volume of the crystal. The normalisation factor comes out to be $N^{-1/2}$ where N is the number of atoms in the crystal.

Similar to the case of one-dimensional lattice, we can find an approximate expression for the energy as follows:

$$E(k) = E_0 + \sum_n \exp(i\mathbf{k} \cdot \mathbf{R}_n) \int \Phi^*(\mathbf{r} + \mathbf{R}_n) [V(\mathbf{r}) - U(\mathbf{r})] \times \Phi(\mathbf{r}) d\mathbf{r} \quad (8)$$

The integral is throughout the volume of the crystal. Neglecting the overlap between nearest neighbouring atoms, the above equation can be written as;

$$E(k) = E_0 - \alpha - \gamma \sum_n \exp(i\mathbf{k} \cdot \mathbf{R}_n)$$

where

$$\alpha = - \int \Phi^*(\mathbf{r}) [V(\mathbf{r}) - U(\mathbf{r})] \Phi(\mathbf{r}) d\mathbf{r}$$

$$\gamma = - \int \Phi^*(\mathbf{r} + \mathbf{R}_n) [V(\mathbf{r}) - U(\mathbf{r})] \Phi(\mathbf{r}) d\mathbf{r}$$

The sum in (8) is over the position vectors of nearest neighbours of the atom at the origin only. Since $\Phi(\mathbf{r})$ is a spherically symmetric function, r is the same for all the nearest neighbours. We may take $V(\mathbf{r})$ to be negative, which implies $V(\mathbf{r}) - U(\mathbf{r})$ would be negative and for s states with small overlap; α and γ are positive.

Let us consider the case of the simple lattice; the vector R_n corresponds to $\pm ae_1, \pm ae_2, \pm ae_3$. Thus, the one-dimensional equations

$$E(k) = E_0 - \alpha - 2\gamma \cos ka$$

can be, in the present case, written as

$$E(k) = E_0 - \alpha - 2\gamma(\cos k_1 a + \cos k_2 a + \cos k_3 a) \quad \text{--- (10)}$$

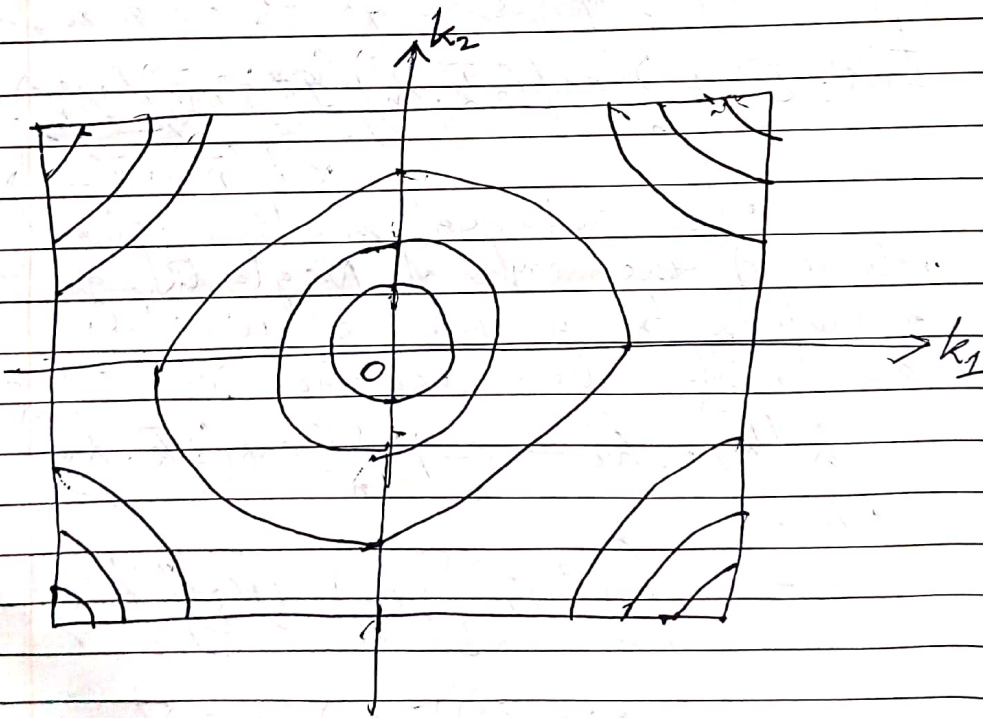
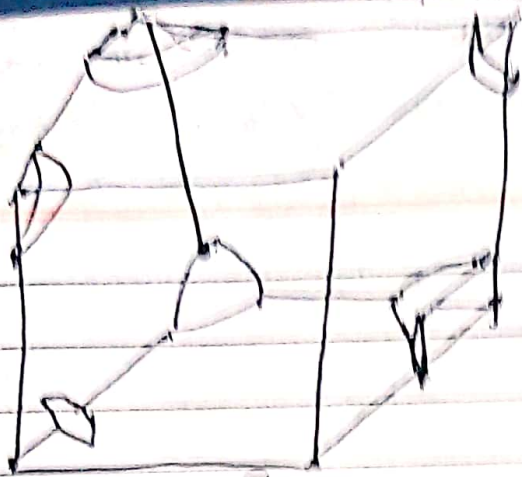


Fig. (1) Energy surfaces as seen through their cross-sections. The various sections are at



(c)

Fig. (2) Energy, E , versus k for the simple cubic lattice in the tight binding approximation. The origin of the k -space is the center of the cube, and the k_x, k_y, k_z axes are parallel to cube edges.

The energy levels are spread over a band of width 12ϵ . It may be noted that the band spread for the one dimensional case was found to be 4ϵ . From Eqn. (10) it is clear that E is simply periodic in function of k , and that all the states are accounted for if k is restricted to be located within a cube bounded by the planes

$$k_x = \pm \pi/a; k_y = \pm \pi/a; k_z = \pm \pi/a \quad (11)$$

The normal derivative of $E(k)$ vanishes on the boundary planes. This can be visualized by differentiating Eqn. (10) which leads to

$$\frac{\partial E}{\partial k_x} = 2\gamma a \sin k_x a = 0 \text{ when } k_x = \pm \frac{\pi}{a} \quad (12)$$

If k_x is small, the Eqn. (10) can be written in an approximate form as

$$E(k) \approx E_0 - \alpha - 2\gamma - 2\gamma \left[\frac{1}{2} (k_x^2 a^2 + k_y^2 a^2 + k_z^2 a^2) \right] \quad (13)$$

Similar to the case of ^{one} dimension, the effective mass near $k=0$, as defined from equation

$$m = \frac{\hbar^2}{2E} k^2, \text{ comes out to be;}$$

$$m^* = \frac{\hbar^2}{2V_0^2} \quad (14)$$

The energy as a function of k along the three axes k_1, k_2 and k_3 is given by the type of curves shown in Fig. (8). The state of the lowest energy is at the centre of the zone. On the other hand, the states of the highest energy are at the corners. Surfaces may be drawn through all points in k -space representing states with the same energy. These are called energy surfaces. Fig. (9) exhibits three representative energy surfaces corresponding to Eqn. (10). Following Eqn. (13), it can be clearly seen that near $k=0$, the surfaces are nearly spheres, as is the case with free electrons. However, as the surfaces get larger, they bulge out more and more towards the centres of the zone faces until eventually they touch, and then intersect the zone boundary. The energy surfaces which intersect the zone boundary do so orthogonally, since the normal derivative of $E(k)$ vanishes on the boundary planes. A cross-section through energy surfaces at equal energy intervals in any one of the coordinate planes is exhibited in Fig. (10).

It must be pointed out that when applied to metals, the tight-binding approximation, is not applicable to the valence or conduction electrons. Instead, it is a reasonable approximation for the electrons in the inner shell. Here simple cubic lattice has been considered only. It, however, turns out that the basic features of the energy surfaces as provided by the simple analysis represent the characteristic features of energy surfaces obtained for real materials. For example, in the actual case the surfaces near the centre of the Brillouin zone are very nearly spheres but they bulge towards the nearest points of the zone boundary as they get larger. It may be recalled that the surfaces are always spheres for free electrons, the amount of bulging clearly depending upon the potential energy function; it would differ even among materials with the same crystal structure.

Density of States